

## GAS-PHASE RATE COEFFICIENTS FOR THE $O(^3P)$ REACTIONS WITH 2-CHLOROPROPENE AND 3-CHLOROPROPENE AT 298K USING THE DISCHARGE FLOW TECHNIQUE

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Received August 26<sup>th</sup>, 2005. In final form September 20<sup>th</sup>, 2005.

Dedicated to the memory of the late Prof. Hans J. Schumacher on the occasion of his 100<sup>th</sup> birthday

### Abstract

The kinetics of the  $O(^3P) + CH_2=CClCH_3$  and  $O(^3P) + CH_2=CHCH_2Cl$  reactions were studied at room temperature in a discharge flow tube system. The overall rate constants based on the measured afterglow reactions were  $(3.15 \pm 0.17) \times 10^{-12}$  and  $(1.35 \pm 0.08) \times 10^{-12}$  in units of  $cm^3 \text{ molecule}^{-1} s^{-1}$ , respectively. The experiments were carried out under pseudo-first-order conditions with  $[O(^3P)]_0 \ll [chloropropene]_0$ . The rate constant for the  $O(^3P) + CH_2=CHCH_2Cl$  reaction is compared with a previous measurement using a different detection technique. This is the first determination of the rate constant of the  $O(^3P) + CH_2=CClCH_3$  reaction. The effect of substituent atoms or groups on the overall rate constants is analyzed in comparison with other propenes in the literature. The correlation of rate constant with the ionization potential of the alkene is also discussed.

### Resumen

En este trabajo se estudió la cinética de las reacciones  $O(^3P) + CH_2=CClCH_3$  y  $O(^3P) + CH_2=CHCH_2Cl$  a temperatura ambiente utilizando un tubo de descarga en flujo acoplado a la técnica de detección por quimiluminiscencia. Se obtuvieron los siguientes valores de constantes de velocidad  $(3,15 \pm 0,17) \times 10^{-12}$  y  $(1,35 \pm 0,08) \times 10^{-12}$  en unidades de  $cm^3 \text{ molécula}^{-1} s^{-1}$ , respectivamente. Los experimentos se realizaron en condiciones de pseudo-primer orden con  $[O(^3P)]_0 \ll [cloropropeno]_0$ . La constante de velocidad para la reacción  $O(^3P) + CH_2=CHCH_2Cl$  se compara con un valor previamente publicado en la literatura utilizando una técnica de detección diferente. La constante de velocidad de la reacción  $O(^3P) + CH_2=CClCH_3$  que se informa en este trabajo constituye la primera determinación cinética de dicha reacción. Se analiza el efecto de átomos o grupos sustituyentes sobre la reactividad de la propenos frente a la reacción con  $O(^3P)$ , así como se correlaciona el potencial de ionización de las olefinas con la constante de velocidad de la reacción.

## Introduction

Halogenated alkenes are volatile organic compounds (VOCs) widely used as degreasing agents and industrial solvents, as well as in the PVC and PVCD industry making up a significant part of disposable wastes [1]. Since large amounts of these compounds are emitted into the atmosphere, it is necessary to investigate how fast these compounds react in the troposphere through a systematic study of the degradation pathways, reaction rate constants and product distributions, thus leading to an evaluation of their environmental impact. [2,3].

Unsaturated hydrocarbons react in the atmosphere with molecules like  $O_3$  or atoms (O, Br, Cl, etc.) or radicals such as OH,  $NO_3$ , etc. The relative importance of these reactions varies depending on the atmospheric conditions [4]. The reactivity of the OH radical with respect to a wide range of species leads to oxidation and chemical conversion of most trace constituents that have an appreciable physical lifetime in the troposphere. The reaction with  $O(^3P)$  atoms although generally not competitive with the other paths because of its low concentration and reactivity, is a prototype system for the addition reactions to the C=C bond. Also, the  $O(^3P)$  atom reactions with the alkenes can become significant in laboratory irradiations of  $NO_x$ -alkene [5].

The gas-phase reactions of ground-state oxygen atoms,  $O(^3P)$ , with alkenes are of both fundamental and practical importance and although the reactions of  $O(^3P)$  with a variety of compounds have been extensively investigated using different experimental methods [6, 7], the literature data base for halogenated alkenes is less comprehensive. Most of these studies have been relative measurements of the rate coefficients [8-13].

As part of a systematic study of  $O(^3P)$  atom reactivity, we report here absolute rate constants for the reactions of  $O(^3P)$  atoms with  $CH_2=CClCH_3$  and with  $CH_2=CHCH_2Cl$  in a conventional discharge flow-tube apparatus at 298 K, in order to obtain absolute values of the reaction rate coefficients for these reactions and to compare these values with previously reported rate measurements when available.

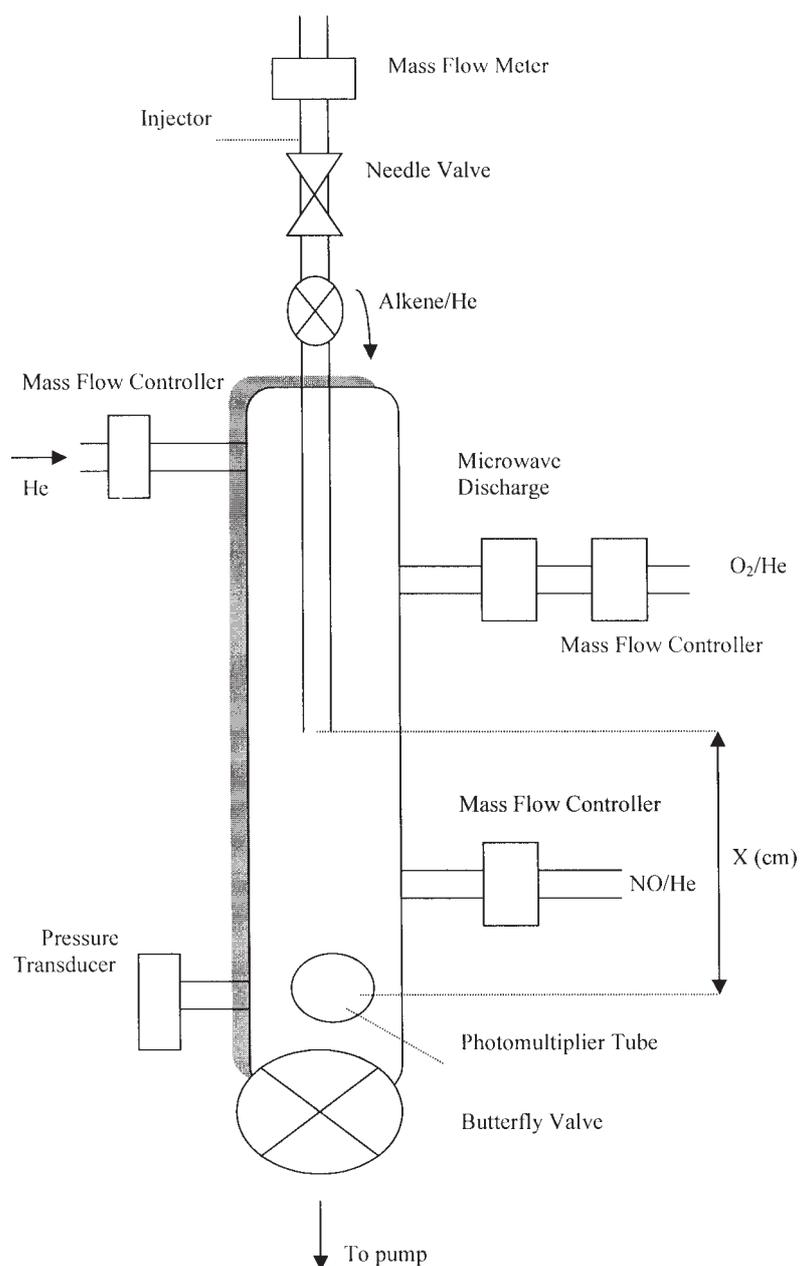
Reliable rate constant values for these reactions are of interest for the role of chemical oxidative processes in atmospheric and combustion chemistry as well as in understanding the effects of halogen substitution on olefin reactivity.

## Experimental

The experiments were conducted in a discharge flow system using the air afterglow chemiluminescence to monitor the oxygen atom concentration (Figure 1). The apparatus has been described previously [14-15]. Briefly, the reactor consisted of a Pyrex tube (1.00 m long and 2.50 cm i.d.) coupled with a sliding injector used to introduce the reactant at one end of the reaction tube.

Oxygen atoms,  $O(^3P)$ , were generated by an electrodeless microwave discharge (30W, 2.5 GHz.) on a 2 %  $O_2$ /He mixture that was slowly flowed through an Evenson cavity and introduced into the main flow of He carrier gas through a fixed side-arm port.

Reaction times could be varied by adjusting the distance of the sliding injector with respect to the fixed position of the photomultiplier tube detector. The position of the injector could be changed from 7.5 to 25 cm from the center of the detection zone, giving contact times in the range of 4.4-14.2 ms. The system was evacuated by a rotary pump ( $90\text{ m}^3\text{ h}^{-1}$ ) and a capacitance manometer (MKS Baratron, 0-10 Torr) was used to measure the pressure in the flow tube.



**Figure 1.** Schematic diagram of the discharge flow-chemiluminescence apparatus used in  $O(^3P)$  atom reaction studies.

Electronic mass flow controllers (MKS 179 A, 1259 C), previously calibrated for each gas mixture, were used to control and measure the gas flows in the reaction tube. Typical linear flow velocities under our experimental conditions were between 1364 and 1750  $\text{cm s}^{-1}$  for the  $O(^3P) + \text{CH}_2=\text{CClCH}_3$  reaction and between 1760 and 1857  $\text{cm s}^{-1}$  for the  $O(^3P) + \text{CH}_2=\text{CHCH}_2\text{Cl}$  reaction.

The experiments were conducted at 298 K and the flow tube pressures were varied in the range of 2.82–4.05 Torr in experiments with  $\text{CH}_2=\text{CClCH}_3$  and from 2.98 to 3.26 Torr with  $\text{CH}_2=\text{CHCH}_2\text{Cl}$ . Helium was used as carrier gas.

The pressure drop along the tube was estimated, considering the viscosity of He, as negligible. The plug-flow conditions [16–17] in the flow tube, allowed us to follow the reaction kinetics of the  $\text{O}(^3\text{P})$  atoms in a known excess of the chloropropene in order to assume the pseudo-first-order approximation.

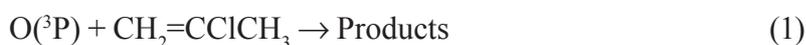
The concentration of  $\text{O}(^3\text{P})$  atoms was monitored by measuring the chemiluminescence from the air afterglow reaction in which  $\text{O}(^3\text{P})$  atoms react with NO to produce electronically excited nitrogen dioxide ( $\text{NO}_2^*$ ) [18]. A constant flow of NO was added 8.5 cm before the photomultiplier tube detector (Hamamatsu R636) so that  $[\text{NO}]$  was *ca.*  $(0.9\text{--}9.8) \times 10^{13}$  molecule  $\text{cm}^{-3}$ , and the chemiluminescence from  $\text{NO}_2^*$  passed through a wide band pass filter ( $\lambda < 500$  nm) before reaching the photomultiplier tube. The output signal,  $S_p$ , of the detector that was proportional to the light intensity of chemiluminescence, was amplified and displayed on an oscilloscope. In all experiments the background signal obtained when  $[\text{NO}] = [\text{chloropropene}] = 0$ , arising from scattered light in the reaction tube, was subtracted from  $S_p$  before further analysis. Concentrations of  $\text{O}(^3\text{P})$  atoms in the kinetic experiments, estimated by the fast reaction with  $\text{NO}_2$  under second-order conditions [19], ranged between  $0.8$  and  $1.7 \times 10^{12}$  atoms  $\text{cm}^{-3}$  and no variations in the obtained results were observed.

## Materials

The commercial gases used in this study had the following stated minimum purity: He (AGA 99.999%),  $\text{O}_2$  (AGA 99.999%), NO (AGA 99.5%),  $\text{CH}_2=\text{CClCH}_3$  (Aldrich 98%) and  $\text{CH}_2=\text{CHCH}_2\text{Cl}$  (Fluka 98%). Nitric oxide was purified by passing it through a trap held at 140 K to remove  $\text{NO}_2$ . Helium was flowed through traps containing silica gel and molecular sieves (BDH Type 5 A) at 77 K, to remove water. Chloropropenes were vacuum-distilled before use and oxygen was used as supplied.

## Results

Using the above mentioned technique the rate constants for the following reactions at 298 K were obtained:



Absolute rate coefficients,  $k$ , for these reactions, were obtained as described below. All the experiments were carried out under pseudo-first-order conditions,  $[\text{chloropropene}]_0 / [\text{O}(^3\text{P})]_0$  always greater than 10.

In the absence of secondary reactions that significantly deplete the transient  $\text{O}(^3\text{P})$  atoms, the concentration of  $\text{O}(^3\text{P})$ ,  $[\text{O}(^3\text{P})]$ , varied in an exponential manner with time:

$$[\text{O}(^3\text{P})]_t = [\text{O}(^3\text{P})]_0 \exp[-(k[\text{chloropropene}]_0 + k_x)t] \quad (3)$$

$$= [\text{O}(\text{}^3\text{P})]_0 \exp (-k' t) \quad (4)$$

$$\ln \{[\text{O}(\text{}^3\text{P})]_0 / [\text{O}(\text{}^3\text{P})]_t\} = k' t \quad (5)$$

where  $[\text{O}(\text{}^3\text{P})]_0$  is the concentration in the absence of chloropropene and  $[\text{O}(\text{}^3\text{P})]_t$  is the concentration after reaction with the chloropropene over time  $t$ ,  $k'$  is the measured pseudo-first-order rate coefficient and  $k_x$  is the first-order rate coefficient for O(<sup>3</sup>P) disappearance by diffusion out of the detection zone, reaction with background impurities or wall losses.

In order to monitor the O(<sup>3</sup>P) concentration, a known excess of NO was added to produce electronically excited NO<sub>2</sub>\* whose global chemiluminescence was checked 8.5 cm downstream of the NO inlet port, following the air afterglow reaction:



If O atoms react via reaction (6) under our experimental conditions, the NO<sub>2</sub> molecules formed rapidly consume O atoms to reform NO via reaction (7) ( $k_{298} = (9.7 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )[20]:



Thus, every time an NO molecule changes to NO<sub>2</sub> in reaction (6), it is almost immediately regenerated by reaction (7). The effect is that the concentration of nitric oxide does not decay along the flow tube. It can be shown that the intensity,  $S$ , of the air afterglow is proportional to the product of the NO and O concentrations. Since [NO] is constant, the intensity of the signal at selected points down the tube is a relative measure of [O(<sup>3</sup>P)].

The first-order kinetic analysis is based on the ratio  $S_0 / S_t$  which is applicable to our system.  $S_0$  is the chemiluminescence signal without reactant and  $S_t$  is the signal after addition of reactant at a fixed time of contact. The O(<sup>3</sup>P) loss between the NO entrance and the detection zone for the reaction with the NO was calculated as less than 4%.

Taking into account the above considerations and equation (5), it is possible to write:

$$\ln (S_0 / S_t) = k [\text{chloropropene}]_0 t \quad (8)$$

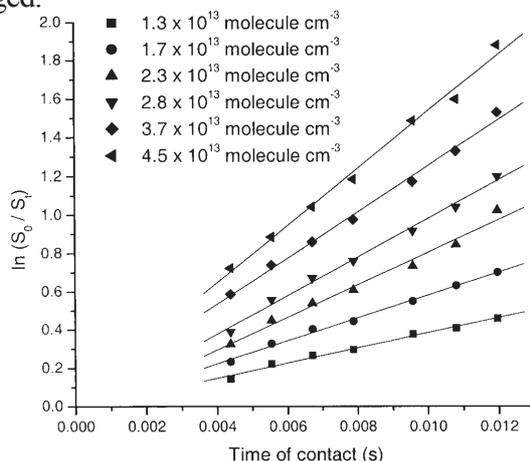
For a specific concentration of chloropropene, the pseudo-first-order decay rate coefficient,  $k'$ , was computed from the slope of a plot of  $\ln (S_0 / S_t)$  as a function of contact time which was linear for approximately three  $1/e$  lifetimes (Figures 2 and 3). The second-order rate constants,  $k$ , for reactions 1 and 2, were obtained from the slopes of the lines of the plots of  $k'$  vs [chloropropene]<sub>0</sub> (Figures 4 and 5). Linear least-squares fits to the data points yield the values of  $k_{(1)} = (3.15 \pm 0.17) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{(2)} = (1.35 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The error limits are one standard deviation from the least-squares analysis and include the 10-20 % uncertainty estimated for possible systematic errors [17]. The pseudo-first-order rate coefficients were corrected for axial and radial diffusion [17], using the following expression:

$$k'_{corr} = k'_{exp} (1 + k'_{exp} D / v^2 + k'_{exp} R^2 / 48 D) \quad (9)$$

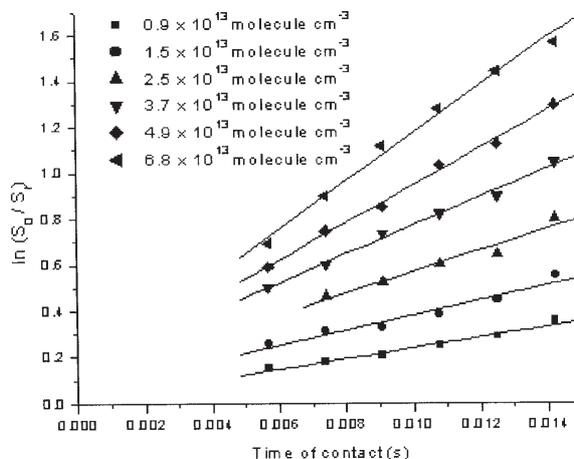
where  $D$  (in units of  $\text{cm}^2 \text{s}^{-1}$ ) is the diffusion coefficient of  $\text{O}(\text{}^3\text{P})$  in He,  $v$  ( $\text{cm s}^{-1}$ ) is the linear flow velocity and  $R$  (cm) is the tube radius. This procedure resulted in  $< 5\%$  upward correction of the  $k'$  values.

The linearity of the data points, especially in the low [chloropropene] $_0$  range in our plots, (Figures 1 and 2) and the same results obtained at different concentrations of O atoms (different [chloropropene] / [ $\text{O}(\text{}^3\text{P})$ ] ratios) suggest that the contribution to the decay of  $\text{O}(\text{}^3\text{P})$  atoms due to secondary reactions with the products of the title reactions is negligible. Also, the fact that the plots show practically no intercepts is consistent with a negligible loss of oxygen atoms by wall reactions ( $k_w = 4\text{-}10 \text{ s}^{-1}$ ), hence no corrections for velocity profile effect were required [17].

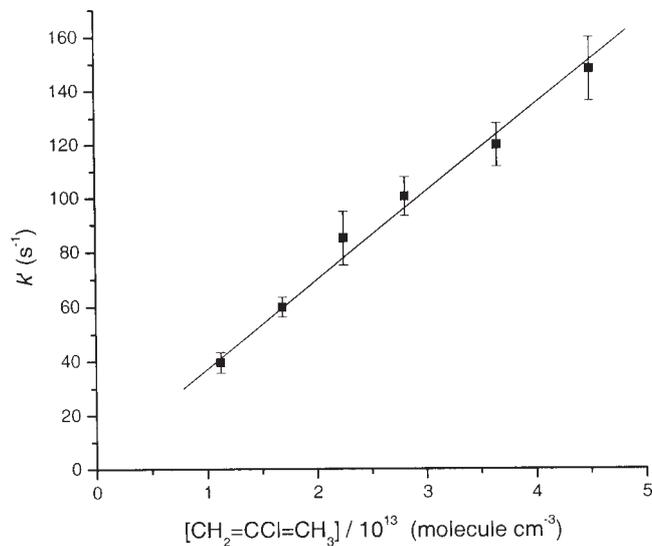
The pressure of the reactor was varied for both reactions and the observed rate constant values remained unchanged.



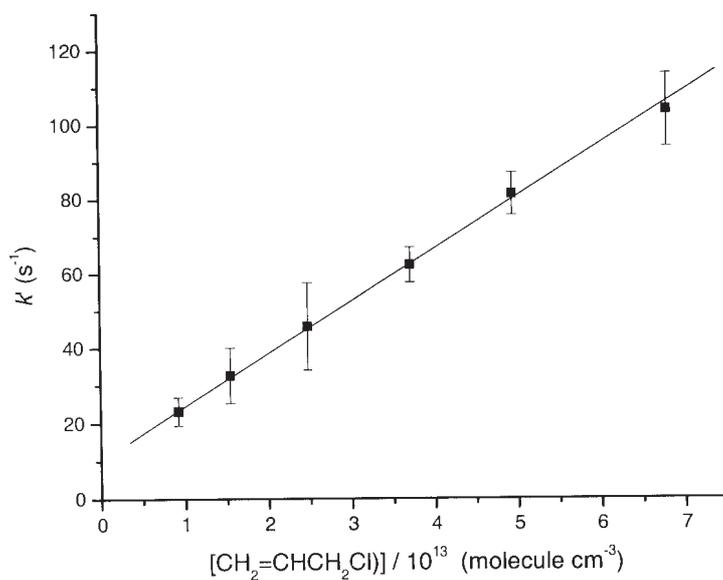
**Figure 2.** Pseudo-first-order plot of the  $\text{O}(\text{}^3\text{P}) + \text{CH}_2=\text{CClCH}_3$  reaction at different concentrations of  $\text{CH}_2=\text{CClCH}_3$ .



**Figure 3.** Pseudo-first-order plot of the  $\text{O}(\text{}^3\text{P}) + \text{CH}_2=\text{CHCH}_2\text{Cl}$  reaction at different concentrations of  $\text{CH}_2=\text{CHCH}_2\text{Cl}$ .



**Figure 4.** Plot of  $k'$  ( $k_{(CH_2=CClCH_3)} + k_x$ ) as a function of  $[CH_2=CClCH_3]$  at 298 K.



**Figure 5.** Plot of  $k'$  ( $k_{(CH_2=CHCH_2Cl)} + k_x$ ) as a function of  $[CH_2=CHCH_2Cl]$  at 298 K.

**Table 1.** Room temperature rate constants of the reaction of halopropenes with O(<sup>3</sup>P) atoms.

Propene	$k_{298K}(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Reference
CH <sub>3</sub> CH=CH <sub>2</sub>	3.99 x 10 <sup>-12</sup>	[7]
CH <sub>2</sub> ClCH=CH <sub>2</sub>	1.35 x 10 <sup>-12</sup>	This work
CH <sub>2</sub> FCH=CH <sub>2</sub>	8.30 x 10 <sup>-13</sup>	[7]
CF <sub>3</sub> CH=CH <sub>2</sub>	3.40 x 10 <sup>-14</sup>	[34]
CF <sub>3</sub> CF=CF <sub>2</sub>	3.00 x 10 <sup>-14</sup>	[14]
CF <sub>3</sub> CCl=CCl <sub>2</sub>	3.32 x 10 <sup>-14</sup>	[34]
CH <sub>3</sub> CCl=CH <sub>2</sub>	3.15 x 10 <sup>-12</sup>	This work
CH <sub>3</sub> CF=CH <sub>2</sub>	1.99 x 10 <sup>-12</sup>	[7]
CH <sub>3</sub> CH=CF <sub>2</sub>	1.82 x 10 <sup>-12</sup>	[7]

## Discussion

The literature database for the reactions of chloropropenes with O(<sup>3</sup>P) atoms is scant [7, 21] as well as with other atmospheric oxidants such as OH radicals [22, 23, 24], O<sub>3</sub> molecules [25, 26] or Cl atoms [27]. There is only one systematic study of the NO<sub>3</sub> degradation reactions with chloropropenes [28-31].

The reaction of CH<sub>2</sub>=CHCH<sub>2</sub>Cl with O(<sup>3</sup>P) atoms was studied previously by Park *et al.* [32] using the discharge flow-mass spectrometry technique and reviewed later by Cvetanovic [7]. The rate constant obtained in the present work for this reaction of 1.35 x 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is in acceptable agreement, within the experimental error, with the recommended value of Cvetanovic of 1.01 x 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> considering an estimated accuracy of around ± 20 % in both cases. To the best of our knowledge, there are no previous kinetic data of the reaction of O(<sup>3</sup>P) atoms with CH<sub>2</sub>=CClCH<sub>3</sub>. Therefore, this is the first determination of the rate constant for this reaction.

An analysis of the rate constants presented in Table 1 for the reaction of halopropenes with O atoms, shows that when one H atom of the propene is replaced by one halogen atom (Cl or F) at any location in the molecule, the reactivity of the alkene towards O(<sup>3</sup>P) atoms decreases relative to that of propene, CH<sub>3</sub>CH=CH<sub>2</sub>. Specifically when one H atom is replaced by Cl or F in the non-olefinic carbon of the propene, the rate constant decreases. The magnitude of the effect is higher in the case of fluorine substitution than when the olefin is chlorinated ( $k_{\text{CH}_3\text{CH}=\text{CH}_2} > k_{\text{CH}_2\text{ClCH}=\text{CH}_2} > k_{\text{CH}_2\text{FCH}=\text{CH}_2}$ ).

A strong decrease in the rate constant (about 2 orders of magnitude), relative to that of propene, is observed when the CH<sub>3</sub> group is replaced by the CF<sub>3</sub> group, so that ( $k_{\text{CF}_3\text{CH}=\text{CH}_2} < k_{\text{CH}_2\text{FCH}=\text{CH}_2} < k_{\text{CH}_3\text{CH}=\text{CH}_2}$ ).

Regarding the substitution in the olefinic carbon atoms, it can be observed in Table 1 that the replacement of one H by Cl or F decreases only slightly the reactivity ( $k_{\text{CH}_3\text{CH}=\text{CH}_2} > k_{\text{CH}_3\text{CCl}=\text{CH}_2} > k_{\text{CH}_3\text{CF}=\text{CH}_2}$ ), whereas the change in reactivity is insignificant once the CH<sub>3</sub> group is replaced by the CF<sub>3</sub> group. Thus,  $k_{\text{CF}_3\text{CH}=\text{CH}_2} \approx k_{\text{CF}_3\text{CH}=\text{CHCl}} \approx k_{\text{CF}_3\text{CF}=\text{CF}_2} \approx k_{\text{CF}_3\text{CCl}=\text{CCl}_2}$ .

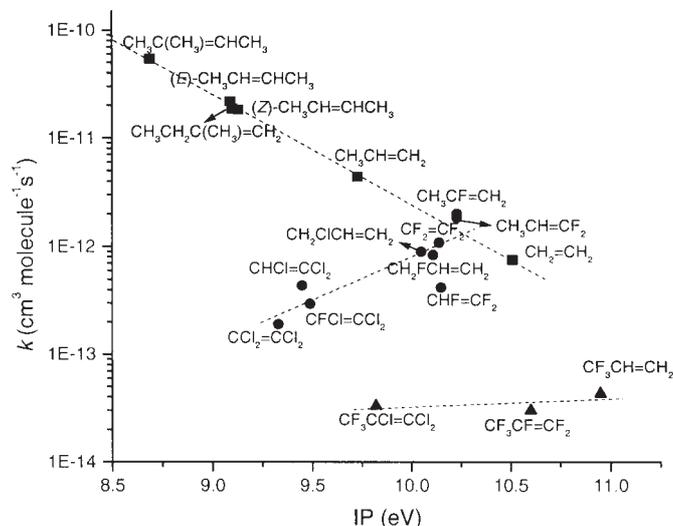
Similar trends are observed for the reactions of NO<sub>3</sub> with halogenated propenes [33] although the rate constants are in general lower due the steric hindrance for the NO<sub>3</sub> electrophilic attack to the double bond.

These results can be rationalized by considering the factors that affect the rate of addition of the electrophilic O(<sup>3</sup>P) atom to the double bond. The strong electron-withdrawing capacity of the F and Cl atoms and the –CF<sub>3</sub> group reduce the charge density on the carbon atoms next to the double bond as well as the polarizability of the π-electrons, leading to a decrease of the rate constants. Substitution of F by Cl, however, would favor an increase of the π-electron density in the double bond through contributions of the chlorine atom lone-pair, thus leading to a smaller decrease of the rate coefficients as F atoms are substituted by Cl.

In general, halogenation of any olefinic carbon atom results in small reactivity decreases in ethenes [14,15] and propenes. However, fluorination of the –CH<sub>3</sub> group in propene results in a more pronounced decrease in O atom reactivity (a factor of 2 orders of magnitude in the case of –CF<sub>3</sub>). Thus, these results of O atom addition studies suggest that halogenation of olefinic carbon atoms does not affect π-electron density in the double bond very much, in contrast with fluorination of the carbon adjacent to the olefinic group in propenes.

The reactivity of O atom addition to alkenes and methyl-substituted alkenes has been found to correlate with the ionization potentials (IP) of the alkenes [35]. The energy required to remove a π-electron, the ionization potential, is lowered in the alkenes by substitution of an H atom by an alkyl group, while the electron density of the double bond is increased by the substitution leading to an increase in the reaction rates. We pointed out previously that the observed correlation between rate constant and IP does not hold for the chloroethenes and chloro-fluoro-ethenes [15, 36] for which the reaction rate constants decrease as the IP decrease. The halogenated propenes follow the same behaviour as can be observed in Figure 6. Worth noting is that the CF<sub>3</sub>-substituted propenes follow the same general trend of the halogenated alkenes but with a different slope which probably reflects the strong electron-withdrawing capacity of the CF<sub>3</sub> group on the double bond, producing a significant reduction of the reactivity of the propene towards attack by the electrophilic O atom.

The reason is probably that in the haloalkenes, the highest occupied molecular orbital (HOMO), whose energy is described by the experimental ionization potential is composed of carbon-carbon π-bonding and halogen-atom lone pairs. Consequently, the HOMO spreads out covering both the double bond and the halogen atom or atoms and the energy of that orbital (the ionization potential) by itself is insufficient to reflect the reactivity of the molecule. The attacking O atom, thus experiences greater non-bonding interactions in the transition state than it does in the alkene reactions where the HOMO is solely carbon-carbon π-bonding [37].



**Figure 6:** Rate constants,  $k$ , for the  $O(^3P)$  reactions as a function of the ionization potential (IP) of the alkenes and methyl-substituted alkenes (■); halogen-substituted alkenes (●); halogen-substituted propenes with the  $CF_3$  group (▲). The dashed lines are not intended to fit the data; they only serve to show a trend.

## Acknowledgment

The authors wish to acknowledge CONICET (Argentina), ANPCyT (Grant BID 1201/OC-AR), Agencia Córdoba Ciencia, SECyT-UNC (Córdoba, Argentina) and Fundación Antorchas (Argentina) for financial support of this research.

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